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ORIGINAL ARTICLE

Preliminary assessment of the ecochemical condition of soils after fertilization of younger spruce *Picea abies* (L.) H. Karst. stands in the Beskid Śląski and Żywiecki Mts.

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Abstract

The experimental plots were located in the middle forest zone (900–950 m) on two nappes of the flysch Carpathians: Magura (the Ujsoły Forest District) and Silesian (the Wisła Forest District) in the spruce stands of age class 21–40 years. Serpentinite was introduced in the autumn of 2008 on all plots while other fertilizers (N, P, NP and NPK) in the spring of 2009. Based on the chemical composition of soil solutions collected in lysimeters placed at the depth of 20 cm in the autumn 2008 and the spring and autumn 2009, ecochemical parameters were calculated: acid neutralization capacity (ANC_{aq}), alkalinity (ALK), the degree of soil acidity (Ma%), acidic cations (Ma), saturation of the exchangeable complex of the soil solid phase (Mb) with alkalis, saturation with alkalis (BS), molar relations Ca/Al, Mb/Al, BC/Al. After the winter, soil solutions became acidic, especially in the Wisła Forest District. The saturation of the studied soils demonstrates moderate flexibility of soils in the Wisła Forest District in relation to acid load, and high flexibility of the Ujsoły soils. The opposite trend was observed for the degree of acidity of soils. Acid neutralization capacity and alkalinity of the waters showed significant variations in soil pH even in the case of small variations in the composition of the solution, if they were caused by the inflow of the anions of NO_3^- and SO_4^{2-}. After application of the fertilizers, an increase of Mg, Ca and Mb was noted in the soil solution, determined in the overlaying highly acidic organic horizons trough the ion-exchange buffering mechanism of highly protonated functional groups with high buffering capacity. Highly improved content of Mg in a soil, and in some cases – also the content of N, P and K, present potential improvement of forest growth capacity without the hazard of adverse side-effects of liming. Aluminum stress in the spruce is unlikely, while trees in the control plots in the Wisła Forest District may already be sensitive.

Key words

ecochemical indicators, slow-realease fertilizers, *Picea abies* stands, mountains

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Introduction

Spruces, mostly in forests of the western part of the Beskidy Mountains, have been subject to intense dying in recent years (Barszcz *et al.* 2009; Barszcz and Małek 2003). Previous studies indicate that sustainability of the forest in this area is particularly at risk in high and medium altitude locations because of difficult site conditions and additional pressure of abiotic, biotic and anthropogenic factors, particularly air pollution, which, combined with long-term effects of the spruce have contributed to acidification of soils (Staszewski *et al.*, 1999; Bytnerowicz *et al.*1999; Małek *et al.* 2005; Małek and Astel 2007).

Both sulphur and nitrogen in the form of NH_4^+ contribute to soil acidification, but deposition of S tends to decrease, whereas N deposition seems to be constant or slightly increasing (Małek and Astel 2007, 2008). Therefore, a role of N in forest dieback becomes an issue of growing concern (van Breemen and van Dijk 1987; Aber 1992; Hornung and Sutton 1995; Flower *et al.* 2007; Sicard *et al.* 2007; Małek 2010).

Together with nutrient loss caused by canopy leaching of K, Ca, Mn and Mg (Ulrich 1983; Bredemeier 1988; Draaijers and Erisman 1995; Draaijers *et al.* 1997; Małek and Astel 2007; Małek 2010), the following properties of precipitation, throughfall, and soil solution become modified: acid neutralising capacity (Reuss and Johnson 1986; Heinrichs *et al.* 1994; Jóźwiak and Kozłowski 2004; Małek and Astel 2008; Małek 2009), alkalinity (Harriman *et al.* 1990; Block *et al.* 2000; Jóźwiak and Kozłowski 2004; Małek and Astel 2008; Małek 2009), soil acidity, and basic cation saturation (Ulrich 1988; Kowalkowski 2002) following soil acidification (Falkengren-Grerup *et al.* 1987), as well as Ca:Al ratio (Cronan and Grigal 1995) and BC:Al ratio (Sverdrup and Warfvinge 1993). These processes may increase tree demand for mineral nutrients, cause nutrient deficiency in the trees and change relations between elements (Cape *et al.* 1990; Zwoliński 2003). The properties listed above can be good ecochemical indicators of forest soil conditions and stand damage from acidification (Block *et al.* 2000; Kowalkowski 2002).

That is why the experiments were located at higher altitudes. It is assumed, that the test results obtained under the difficult conditions of these altitudes may, if necessary, be used also at lower altitudes above sea level.

Because of differences between the sites, caused by the geological structure of the research area, the experimental plots were set up in the areas of two Carpathian nappes, diversified in terms of lithological deposits:

– The Magura Nappe (the Ujsoły Forest District, precinct Ujsoły), built of thin-bedded sandstone with a share clay-marly slate inclusions, producing clayey waste-mantle with meso/eutrophic soils, more buffered, more resistant to degradation;
– The Silesian Nappe (the Wisła Forest District, Wisła precinct) in the range of Barania Góra mountain, built from the lower Istebna layers, consisting of thick-bedded sandstones and conglomerates producing sandy-clayey waste-mantle with oligotrophic soils, which are susceptible to degradation (Małek *et al.* 2008).

The aim of the study is to present preliminary assessment of the effects of total-area fertilization of soil with serpentinite in combination with N, P and K in the light of ecochemical indicators.

Materials and methods

The experimental plots were located in the middle forest zone (900–950 m a.s.l.) on two nappes of the flysch Carpathians: Magura (the Ujsoły Forest District, precinct Ujsoły) and Silesian (the Wisła Forest District, precinct Wisła) in the range of Barania Góra mountain, in the spruce stands of age class 21–40 years. The following variants: C – control – no fertilizer; S – ground serpentinite (2000 kg/ha in the Ujsoły Forest District, 4000 kg/ha in the Wisła Forest District) SN – serpentinite + nitrogen (440 kg ammonium nitrate (34%N)/ha (150 kg N/ha); SP – ground serpentinite + P (400 kg of granulated triple superphosphate 20% P)/ha; SNP – ground serpentinite + NP (440 kg ammonium nitrate/ha – 150 kg N/ha and 400 kg of granulated triple superphosphate/ha – 80 kg P/ha); SNPK; ground serpentinite + NP (as above) + K (250 kg of potassium sulphate 44% K/ha – 110 kg K/ha. Serpentinite was introduced in the autumn 2008, and other fertilizers in the spring of 2009.

Aggregate samples for laboratory testing were collected on the experimental areas in Ujsoły and Wisła on 17 August 2009, from five plots of different nutrition treatment variants as well as from reference plots where no nutrition treatment was applied. The samples

were collected from the organic horizon (without further subhorizons) and from the mineral horizon down to 20 cm in depth. The analyses covered the total of 72 soil samples, 36 collected in each of the two study sites in Wisła and Ujsoły.

The samples collected were first dried at room temperature to an air-dry condition and then sieved through a 2 mm sieve. The analysis of sample parameters included:

– soil pH in H_2O and 1M KCl solution, determined potentiometrically, with soil-to-solvent proportion of 1:2.5 for mineral soils and 1:5 for organic soils (Tab. 1);
– exchangeable acidity (H_w) and exchangeable aluminium (H_{Al}), determined by the Sokołow method (Tab. 1);
– calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) (base exchange capacity – S) in a 1M CH_3COONH_4 extract of pH 7.0 as determined with a Thermo Scientific* iCAP 6000 ICP OES Spectrometer, with calculation of effective cation exchange capacity T_e (total of S and H_w) and the saturation of the effective base saturation V_e% ($S/T_e \cdot 100$) (Tab. 1);
– the computed values were the percentages of exchangeable calcium and magnesium in T_e, the molar proportions of the said exchangeable calcium and magnesium forms, the proportion of the total of exchangeable calcium, magnesium and potassium to exchangeable aluminium, and the proportion of exchangeable calcium to exchangeable aluminium (Tab. 1)

The analysis of soil solution chemical composition was conducted on each experimental plot, based on soil lysimeters, which were gravitational and not insulated (L-20), placed at the depth of 20 cm. Their purpose was to penetrate, both horizontally and vertically, the upper layers of soil. They were installed in 3 replications in each variant of the experiment, prior to the application of fertilizers in September 2008. The surface of each lysimeter was 0.077 m^2. Each lysimeter was connected, by means of a plastic tube, with the collection container (plastic canister, chemically neutral), placed in mineral soil (ICP-Forest Manual 1998; Małek 2009).

The results obtained were used to calculate the ecochemical soil indices: $ANC_{aq,}$ ALK, Ma, MB, BS, Ca/Al, BC/Al – Tab. 2 (Kowalkowski 2002; Małek 2009).

Sampling was conducted at the beginning (on 30April) and the end (on 30 October) of the vegetation period 2009. The pH and conductivity were measured directly at the place of sampling, using equipment produced by Eijkelkamp company: pH 13.37 and EC 18.34.

Water samples were analyzed in the laboratory using ion chromatography (Dionex-320, Sunnyvale, CA, USA) to determine the concentration of ions: Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, F^-, NH_4^+, Na^+, K^+, Ca^{2+} i Mg^{2+} Al^{3+} and the ICP OES technique in order to determine the concentrations of the following elements: Fe, Mn, Zn and Ni. Analyzed in parallel was reference material containing the certified content of analytes. A sample of water with low pH from southern Ontario (Canada), RAIN.97 – No. 409th, was used for this purpose.

Acid neutralization capacity (ANC_{aq}) (Reuss and Johnson, 1986, Heinrichs *et al.* 1994), alkalinity (ALK) (Harriman *et al.*, 1990, Block *et al.*, 2000), the degree of soil acidity (Ma%) (Ulrich 1988), the acidic cations (Ma), saturation of the exchangeable complex of the solid soil phase with alkalis (Mb), saturation with alkalis (BS) (Kowalkowski 2002), molar relations Ca:Al (Cronan and Grigal 1995), and BC: Al (Sverdrup and Warfvinge 1993) were assessed using the following formulas:

$$ANC_{aq}\ (\mathrm{meq} \cdot \mathrm{dm}^{-3}) = K^+ + Na^+ + 2Mg^{2+} + 2Ca^{2+} - NO_3^- - Cl^- - 2SO_4^{2-}$$

$$ALK\ (\mathrm{mmol} \cdot \mathrm{dm}^{-3}) = (K^+ + Na^+ + Mg^{2+} + Ca^{2+}) - (NO_3^- + Cl^- + SO_4^{2-})$$

$$Ma\% = (Ma + H^+)/(Ma + Mb + H^+) \cdot 100$$

$$Ma\ (\mathrm{mmol} \cdot \mathrm{dm}^{-3}) = (Mn^{2+} + Fe^{2+} + Al^{3+})$$

$$Mb\ (\mathrm{mmol} \cdot \mathrm{dm}^{-3}) = (K^+ + Na^+ + Mg^{2+} + Ca^{2+})$$

$$BS(\%) = (K^+ + Na^+ + Mg^{2+} + Ca^{2+})/(K^+ + Na^+ + Mg^{2+} + Ca^{2+} + Mn^{2+} + Fe^{2+} + Al^{3+} + H^+) \cdot 100$$

$$Ca : Al = Ca^{2+}/Al^{3+}$$

$$BC : Al = (K^+ + Mg^{2+} + Ca^{2+})/Al^{3+}$$

The distributions of the soil parameters determined for the analysed nutrition treatment variants were then compared by means of a non-parametric Kruskal-Wallis test (Łomnicki 1995). We also calculated Pearson's correlation coefficients between the properties of soil samples collected and the properties of soil solution collected at 20 cm depth. Test were applied for water data after fulfilling the conditions of normality of distribu-

Tab. 1. Some physico-chemical properties of surface horizons of soils of research plots exposed to total-area fertilization (CP) in stands of age class 21–40 years in the Wisła and Ujsoły Forest Districts (mean values from 3 replications)

CP	pH in		S	Al^{3+}	H^{+}	T_e	Ca^{2+}	Mg^{2+}	Deegre of base saturation %	Ca^{2+}/Mg^{2+}	$(Ca^{2+} + Mg^{2+} + K^{+})/(Al^{3+})$	Ca^{2+}/Al^{3+}
	H_2O	1M KCl	cmol kg^{-1} of soil				% in T_e					
Wisła Forest District												
Ofh horizons												
C	3.5	2.71	3.21	21.35	6.44	31.00	5.04	1.91	10.46	2.64	0.15	0.07
S	3.71	2.81	5.62	20.60	4.60	30.82	5.53	9.30	19.31	0.59	0.27	0.08
SN	3.74	2.75	5.78	20.79	6.18	32.75	6.00	8.24	17.73	0.73	0.27	0.09
SP	3.70	2.83	8.09	18.20	5.55	31.84	10.67	10.58	25.52	1.01	0.44	0.19
SNP	3.75	2.82	7.23	17.83	5.02	30.08	13.83	7.03	24.89	1.97	0.40	0.23
SNPK	3.55	2.71	7.30	21.65	6.35	35.30	9.20	7.86	20.76	1.17	0.33	0.15
AE horizons												
C	3.66	2.71	0.30	6.24	0.90	7.44	1.28	1.14	4.11	1.13	0.05	0.02
S	3.50	2.78	0.42	8.66	0.64	9.72	1.15	1.75	4.56	0.66	0.05	0.01
SN	3.57	2.72	0.36	5.21	1.00	6.58	1.49	2.05	5.65	0.73	0.07	0.02
SP	3.62	2.82	0.43	9.86	0.80	11.10	1.36	1.27	3.99	1.07	0.04	0.02
SNP	3.50	2.79	0.58	7.51	0.79	8.88	3.10	2.01	7.80	1.54	0.07	0.04
SNPK	3.45	2.63	0.51	9.83	0.93	11.27	1.37	1.51	5.18	0.91	0.05	0.02
Ujsoły Forest District												
Oh horizons												
C	4.35	3.41	11.26	11.60	2.01	24.86	36.96	5.26	11.6	7.02	0.96	0.79
S	5.12	3.91	14.87	4.01	0.86	19.74	56.83	1514	4.01	3.75	3.68	2.80
SN	4.53	3.69	16.30	9.57	1.47	27.34	46.22	10.28	9.57	4.50	1.70	1.32
SP	5.07	4.27	22.07	2.94	0.91	25.92	67,52	12.64	2.94	5.34	7.36	5.95
SNP	5.17	4.25	19.35	3.90	0.84	24.08	64,42	12.89	3.90	5.00	4.95	3.98
SNPK	4.96	4.03	19.63	4.48	0.96	25.07	58,89	15.59	4.48	3.78	4.37	3.30
A horizons												
C	4.46	3.46	3.64	12.79	0.43	16.86	17.06	2.74	12.79	6.23	0.28	0.22
S	4.75	3.64	4.86	8.27	0.21	13.35	27.82	6.04	8.27	4.61	0.58	0.45
SN	4.30	3.50	4.17	11.90	0.46	16.53	18.50	4.51	11.9	4.10	0.35	0.26
SP	4.91	3.88	7.65	5.22	0.24	13.11	46.16	9.08	5.22	5.08	1.46	1.16
SNP	4.83	3.90	7.56	5.23	0.21	13.01	47.84	7.70	5.23	6.21	1.44	1.19
SNPK	4.45	3.59	4.40	8.01	0.21	12.62	26.70	5.60	8.01	4.77	0.54	0.42

tion of a variable in groups (sets) and the equality of variance in groups – by means of the t-Student test and, if even one of the conditions was not met – by means of the non-parametric U-Mann-Whitney. Sstatistical tests were performed with Statistica 8 software package.

Results and discussion

During the first year following the nutrition treatment, no statistically significant impact of different nutrition treatment variants was observed in the two uppermost

horizons of the soils analysed based on the soil analysis. This probably results from high variability of soil properties in the top horizons and the low number of repetitions (the experiment was repeated three times). However, the results obtained are indicative of some tendencies in the soil transformation processes within the treated plots as compared with the reference, non-treated ones (Tab. 1).

In comparison with the O horizons of reference plots, the overlaying O horizons of treated plots (both in Wisła and in Ujsoły, respectively) show positive changes in soil properties increased pH_{H2O} (by 0.19 and 0.62 pH unit) and pH_{KCl} (by 0.07 and 0.04 pH unit about twofold increase in the total of base cations (by 3.6 and 7.2 cmol · kg^{-1} of soil); lower concentrations of exchangeable aluminium (by 1.5 and 6.6 cmol · kg^{-1}); lower concentrations of exchangeable hydrogen (by 0.9 and 1.01 cmol · kg^{-1}); significantly higher base saturation (by 11.1% and 29.3%); higher content of exchangeable calcium (by 6.2% and 26.6%, particularly marked in the plots treated with superphosphates) and of exchangeable magnesium (by 6.7% and 8.0%) in the sorption complex higher proportion of the total of exchangeable calcium, magnesium and potassium to exchangeable aluminium (the change being respectively 0.15→0.34 and 0.96→4.4); higher molar proportion of exchangeable calcium to exchangeable aluminium 0.07→0.19 and 0.79→3.47);as well as lower molar proportion of exchangeable calcium to exchangeable magnesium 2.64→1.09 and 7.02→4.7) (Tab. 1).

At the experimental area in Wisła, the humic-eluvial horizons of treated plots, as compared with non-treated ones, show both positive and adverse changes in soil properties. The adverse changes include decreased pH_{H2O} (by 0.13 pH unit) and increased exchangeable aluminium content (by 2 cmol · kg^{-1}), while the positive changes are lower concentrations of exchangeable hydrogen (by 0.07 cmol · kg^{-1}increased base exchange capacity (by 0.16 cmol · kg^{-1} cation exchange capacity (on average by 2.1 cmol · kg^{-1}), higher base saturation (on average by 1.3%),slightly higher content of exchangeable Ca (on average by 0.41%) and exchangeable Mg (on average by 0.46%) in the effective cation exchange capacity, as well as a slightly lower molar proportion of exchangeable calcium capacity to exchangeable magnesium capacity (1.13→0.98) (Tab. 1).

At the experimental area in Ujsoły, the humic-mineral A horizons of treated plots, as compared with non-treated ones, show positive changes in nearly all properties, i.e. increased: pH_{H2O} and in pH_{KCl} (respectively by 0.19 and 0.24 pH unit) and cation exchange capacity (on average 3.6→5.7 cmol · kg^{-1}), as well as lower concentrations of exchangeable aluminium (on average by 5 cmol · kg^{-1}) and exchangeable hydrogen (by 0.27 cmol · kg^{-1}), higher base saturation (doubled on average), higher proportion of exchangeable Ca (on average by 23%) and exchangeable Mg (on average by 3.85%), higher molar proportion of exchangeable Ca, Mg and K capacity to exchangeable aluminium (0.28→0.87), higher molar proportion of exchangeable Ca capacity to exchangeable Al capacity (the change being on average 0.22→0.70), as well as lower molar proportion of exchangeable Ca capacity to exchangeable Mg capacity (the change being on average 6.23→4.95) (Tab. 1). The only adverse change related to nutrition treatment was a decrease in cation exchange capacity (on average by 3.14 cmol · kg^{-1}) (Tab. 1).

A significant negative correlation ($R = –0.82$, $p < 0.05$) was found between the pH of the soil solution collected at 20 cm and the base saturation of O_{fh} horizon at the experimental area in Wisła, as well as between the pH of the soil solution and the base exchange capacity of O_h horizon ($R = -0.83$, $p < 0.05$) at the experimental area in Ujsoły (Tab. 3). At the experimental area in Wisła we found a positive correlation between the pH_{H2O} at the O_{fh} horizon and soil acidity (Ma%), as computed from the proportion between the total acid cation capacity and the total acid and base cation capacity in the soil solution collected at 20 cm, as well as a negative correlation ($R = –0.82$, $p < 0.05$) between the pH_{H2O} at the O_{fh} horizon and base saturation, as computed on a basis of the soil solution (BS),and a negative correlation ($R = -0.82$, $p < 0.05$) between the pH in H_2O at the O_{fh} horizon and the molar proportion of base cation (Ca^{2+}, Mg^{2+} and K^+) capacity to the exchangeable aluminium in the soil solution collected at 20 cm. Additionally, at the experimental area in Wisła we found a positive correlation between base saturation of the O_{fh} horizon and properties of the soil solution at 20 cm, including base cation capacity (Mb) and the molar proportions of Ca : Al and Mb : Al. The value of correlation between the pH of the soil solution and pH H_2O

Tab. 2. Indicators of ecochemical soil condition in the light of the results of analysis of soil solutions collected in spring and autumn 2009 from research plots exposed to total-area fertilization (CP) in stands of age class 21–40 years in the Wisła and Ujsoły Forest Districts

Variant of fertilization	pH	BS	ANC_{aq}	ALK	Ma	Mb	Ma%	Ca / Al	Mb / Al	BC / Al
			meq L^{-1}	mmol L^{-1}						
Wisła Forest District										
Spring										
C	3.55	24.95	–9.114	–8.838	0.042	0.108	75.047	1.15	3.30	24.95
S	3.42	23.27	–8.798	–8.662	0.042	0.128	76.726	1.54	4.00	23.27
SN	3.41	22.64	–9.204	–8.882	0.041	0.126	77.358	1.42	3.90	22.64
SP	3.43	23.04	–9.040	–8.781	0.041	0.124	76.956	1.31	3.83	23.04
SNP	3.42	23.34	–9.090	–8.839	0.040	0.128	76.657	1.45	4.21	23.34
SNPK	3.41	22.08	–9.116	–8.840	0.044	0.123	77.919	1.20	3.62	22.08
Autumn										
C	3.58	27.86	–9.143	–8.869	0.040	0.117	72.141	1.23	3.78	27.86
S	3.35	22.04	–9.096	–8.966	0.043	0.138	77.964	1.66	4.28	22.04
SN	3.36	22.52	–9.793	–9.481	0.042	0.139	77.484	1.65	4.29	22.52
SP	3.34	21.91	–10.335	–9.790	0.041	0.140	78.089	1.72	4.46	21.91
SNP	3.38	23.46	–9.781	–9.541	0.044	0.141	76.538	1.68	4.38	23.46
SNPK	3.39	23.94	–9.830	–9.568	0.043	0.142	76.059	1.66	4.38	23.94
Ujsoły Forest Fistrict										
Autumn										
C	4.40	73.25	–7.085	–6.878	0.026	0.180	26.748	5.33	11.43	73.25
S	4.37	74.36	–7.178	–7.116	0.028	0.204	25.636	5.74	11.98	74.36
SN	4.31	73.22	–7.814	–7.574	0.027	0.209	26.778	6.34	13.07	73.22
SP	4.32	73.67	–8.064	–7.589	0.026	0.207	26.327	6.43	13.20	73.67
SNP	4.30	73.25	–7.609	–7.441	0.026	0.207	26.755	6.47	13.34	73.25
SNPK	4.29	73.01	–7.736	–7.546	0.026	0.209	26.990	6.61	13.67	73.01

of the O_{fh} horizon at the experimental area in Wisła was also close to a negative statistical significance We found no significant correlations between properties of the soil solution collected at 20 cm and properties of the soil mineral horizons at the experimental areas either in Wisła or in Ujsoły (Tab. 3).

The base cations released from the nutrients spread over the highly acidic soils caused extraction of acidic cations from the overlay humus horizon. Thus, the proportion of acidic cations in the soil solution increased while the pH of the upper mineral horizon decreased. These significant negative correlations found between the soil solution at 20 cm and the properties of O_{fh} horizon at the experimental area in Wisła are indicative of the high neutralising capacity of the overlay humus horizon with regard to the bases of protonized function groups. This is confirmed by the experiment conducted over an experimental area with an overlay humus horizon, located in Höglwald (South Bavaria, Germany), where changes in soil properties resulting from liming were observed solely within the overlay humus horizon, and no changes in the underlying mineral horizons occurred within seven years from liming (Kreutzer 1995).

In order to improve the magnesium content in soil and to avoid the adverse effects of forest soil liming (Kreutzer 1995; Misson *et al.* 2001; Lundström *et al.* 2003), the nutrient applied was ground serpentinites, thus the use of carbonates was avoided. It was decided

Tab. 3. Correlation matrix of soil solution and soil properties of younger spruce stands on experimental plots at Wisła and Ujsoły Forest Districts

Properties of soil solution	Properties of soil horizons						
	pH in H_2O	pH in KCl	S	V_e%	Exch. Al^{3+}	$(K^{+}+Mg^{2+}+Ca^{2+})/Al^{3+}$	Ca^{2+}/Al^{3+}
Wisła Plot							
Ofh Horizon							
pH	–0.79	–0.64	–0.81	*–0.82*	0.43	–0.75	–0.42
Ma%	*0.82*	0.69	0.74	0.76	–0.43	0.69	0.33
Mb	0.66	0.49	*0,89*	*0.86*	–0.39	0.80	0.57
BS(%)	*–0.82*	–0.69	–0.74	–0.77	0.43	–0.69	–0.33
Ca^{2+}/Al^{3+}	0.74	0.62	*0.89*	*0.89*	–0.48	*0.83*	0.56
Mb/Al^{3+}	0.66	0.59	*0.95*	*0.93*	–0.52	*0.89*	0.66
BC/Al^{3+}	*–0,82*	–0.69	–0.74	–0.77	0.43	–0.69	–0.33
AE Horizon							
pH	0.53	–0.36	–0.53	–0.25	–0.42	–0.11	0.02
Ma%	–0.42	0.45	0.41	0.16	0.37	0.06	–0.12
Mb	–0.71	0.15	0.72	0.43	0.47	0.20	0.17
BS(%)	0.42	–0.45	–0.41	–0.16	–0.37	–0.06	0.12
Ca^{2+}/Al^{3+}	–0.60	0.31	0.66	0.35	0.48	0.12	0.11
Mb/Al^{3+}	–0.58	0.28	0.71	0.34	0.56	0.06	0.18
BC/Al^{3+}	0.42	–0.45	–0.41	–0.16	–0.37	–0.06	0.12
Ujsoły Plot							
Oh Horizon							
pH	–0.46	–0.68	*–0.83*	–0.60	0.51	–0.51	–0.49
Ma%	–0.42	–0.13	0.12	–0.30	0.38	–0.22	–0.21
Mb	0.66	0.73	0.78	0.76	–0.69	0.58	0.55
BS(%)	0.42	0.13	–0.12	0.30	–0.38	0.22	0.21
Ca^{2+}/Al^{3+}	0.52	0.75	*0.90*	0.69	–0.59	0.62	0.61
Mb/Al^{3+}	0.50	0.74	*0.88*	0.66	–0.56	0.59	0.58
BC/Al^{3+}	0.42	0.13	0.12	0.30	–0.38	0.22	0.21
A Horizon							
pH	–0.04	–0.44	–0.43	–0.57	0.53	–0.44	–0.44
Ma%	–0.53	–0.19	–0.15	–0.09	0.21	–0.10	–0.09
Mb	0.21	0.48	0.44	0.55	–0.59	0.42	0.41
BS(%)	0.53	0.19	0.15	0.09	–0.22	0.11	0.09
Ca^{2+}/Al^{3+}	0.14	0.52	0.51	0.64	–0.61	0.52	0.51
Mb/Al^{3+}	0.12	0.51	0.50	0.64	–0.60	0.51	0.51
BC/Al^{3+}	0.53	0.19	0.15	0.09	–0.22	0.11	0.09

Correlations coefficients in *italic* means $p < 0.05$

that there is no need to introduce additional calcium into soil, which would intensify the calcium/magnesium antagonism while the soils and forest stands in question were found to suffer from magnesium deficits (Małek 2010). The only significant and permanent effect of the introduction of dolomites into spruce stand soils at the experimental area in Höglwald (Southern Bavaria) was found in Ca concentrations in coniferous needles, with Mg concentrations not rising in parallel, although Ca and Mg contents in the dolomite were equivalent (Huber *et al.*, 2004). The physiological demand for calcium is relatively low, especially in coniferous trees. Besides, calcium uptake through the roots is generally the passive process, and therefore plants cannot avoid excessive uptakes of Ca, which must be reduced to calcium oxalates (Gülpen *et al* 1995; quoted after Huber *et al.* 2004).

The inclusion of nitrogen treatment variants into the experiment resulted from the need to test the hypothesis of forest environment being oversaturated with nitrogen (Binkley and Hogberg 1997), while the inclusion of potassium treatment variants was related to the potassium deficits – suffered by tree stands as a result of soil liming (Misson *et al.* 2001).

The indicators of the ecochemical soil conditions, identified on a basis of analytical results of the soil solution collected in the spring and autumn of 2009 at the research plots in both forest divisions, are presented in table 2. Obtained results are not statistically significant, but indicate the effect of fertilizing after winter and the vegetation period.

In the stands of age 21–40 years, water penetrating the 20 cm soil layer treated with serpentinite, after the winter period, was further acidified, especially in the Wisła Forest District. A similar situation was observed in young stands in the catchment of the Dupniański stream (Małek 2009). Soil acidification increased after the vegetation period. In the Ujsoły Forest District, soil pH also decreased (in comparison with the higher input values), but only slightly. The dominant process of buffering in the Wisła Forest District is the dissolution and complexation of metal hydroxides (Fe and Al buffer) while in the Ujsoły Forest District it is the release of Al from the crystal lattice of aluminosilicates (buffer ion) – cf. Kowalkowski (2002).

Saturation with alkalis (BS) in the analyzed waters was very small, especially in the Wisła Forest District, and it even decreased slightly after the application of fertilizers, especially after the addition of nitrogen in the spring 2009. In the waters of the Ujsoły Forest District, the BS level was, however, more than 3 times higher than that of the Wisła Forest District. The relevant values obtained in the Wisła Forest District indicate moderate elasticity of water solutions (after their passage through the surface layer of soil) in relation to the acid load – just as it was noted under stands of age 21–40 years in the catchment of the Dupniański stream (Małek 2009), while the values obtained in the Ujsoły object reveal high elasticity of these solutions.

The opposite trend was observed for the degree of soil acidity: Ma% (according to Ulrich 1988), defined by analyzing the water passing through soils. The obtained values for this characteristic of water from the Wisła object indicate acidity class 1 (very acidic soil) – as in the catchment of the Dupniański stream (Małek 2009) – while the values of Ma% in Ujsoły indicate class 3, i.e. slightly acid soil. Fertilization did not change these values considerably, despite a significant increase in the alkali saturation of the exchangeable complex of the solid soil phase (Mb) and the maintenance of acidic cations (Ma) at the same level.

The acid neutralization capacity (ANC_{aq}) and the alkalinity of the analysed waters in both locations ranged from $-7 \div -10$ $mmolL^{-1}$ on the experimental plots with trees in studied age class, which practically places them near the 0 value of the applied scale. Soil solutions with such alkalinity react with strong fluctuations of the pH values, even to the slightest change in the composition of the solution, if caused by the inflow of NO_3^- and SO_4^{2} anions, since in this respect there is no buffering associated with the release of Al from the solid soil phase (low saturated with alkalis) from which it is released (Kowalkowski 2002).

Analyzing the molar relations (Ca/Al, Mb/Al, BC/Al) in the water obtained in the lysimeters at the experimental plots in spruce stands, an increase was observed in Ca and Mb after the application of fertilizers. The Ca/Al relations reached the normal values (> 1.5), at which the aluminum stress in the spruce is unlikely, while the trees of this species in the control plots in the Wisła object may already be sensitive (Ca/Al : 1.0–1.5). The obtained results indicate that for younger spruce trees in the Ujsoły Forest District this stress is unlikely.

Conclusions

- After winter, soil solutions (collected at the depth of 20 cm) became acidic, especially in the Wisła Forest District. Both the experiment results and a literature review on the nutrition treatment rich in base cations prove that the properties of soil solution in the upper mineral horizons of forest soils are determined in the overlaying highly acidic organic horizons trough the ion-exchange buffering mechanism
- Alkali saturation (BS) of the studied soils, evaluated based on properties of analysed waters, was very low, especially in the Wisła Forest District, and decreased slightly after the application of fertilizers in the spring 2009, whereas in the Ujsoły Forest district it was more than 3 times higher when compared with the Wisła Forest District. This demonstrates moderate elasticity of the Wisła Forest District soils in relation to the acid load as compared to high elasticity of the Ujsoły Forest District soils. The opposite trend was observed for the degree of acidity of soils (Ma%).
- The acid neutralization capacity ($ANC_{aq)}$) and the alkalinity (ALK) of the analysed waters in both locations places them near the “0” value, causing significant variations in the soil pH even in response to small variations in the composition of the solution, if they are caused by an inflow of NO_3^- i SO_4^{2-} anions. After the application of the fertilizers an increase of Ca and Mb was noted in soil solutions.
- The values of the Ca/Al relations of analysed waters reached the normal level (> 1.5), at which the aluminum stress in the spruce is unlikely, while trees in the control plots from the Wisła Forest District may already be sensitive (Ca/Al ranging from 1.0 to 1.5), and the application of fertilizers also improved their value.
- The treatment applied only slightly affected the physical and chemical properties of the analysed soils, highly improved their magnesium content, and in some of them, also the content of nitrogen, phosphorus and potassium, which present potential improvement in forest growth capacity without the hazard of adverse side-effects of liming.

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